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wge **Working Group on Effects of the Convention on Long-range Transboundary Air Pollution**

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Photo: A view from the ICP IM site Gårdsjön, Sweden

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Contents

List of Acronyms

ANC	Acid neutralising capacity
EMEP	Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
CCE	Coordination Center for Effects
CEC	Cation exchange capacity
CIAM	Centre for Integrated Assessment Modelling
CLE	Current legislation scenario
FAB	First-order Acidity Balance model
ICP IM	International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems
ICP Waters	International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes
MAGIC	Model of Acidification of Groundwaters In Catchments
NFP	National Focal Point
SSWC	Steady-State Water Chemistry model
UN ECE	United Nations Economic Commission for Europe

Summary

Dynamic models can provide a key input to the forthcoming assessment of the Gothenburg Protocol and for input to any further emission reduction agreements by establishing the time-scale of the ecosystem recovery from acidification. Dynamic models of acidification are currently well developed and represent a demonstration of the use of such tools within the Convention. The ICP IM plays a key role in this activity by providing detailed and consistent physical and chemical data and long-time series of observations of input and output fluxes for key sites against which model performance can be assessed and key uncertainties identified. Data from six ICP IM sites have been used here to test the MAGIC model predictions against several years of observations and to make predictions into the future (2030) assuming the agreed emission reductions under current legislation plans (essentially the Gothenburg Protocol) and the Oslo Protocol are achieved by 2010. In addition, uncertainties in data and model structures are assessed.

Usually, the model prediction matches the long-term observation at each of the sites. The large declines in sulphate (SO_4) concentrations seen at many of the sites are well captured by the model, as are the observed increases in acid neutralising capacity (ANC). At some sites, sea-salt inputs vary considerably on an annual basis causing the match between observed and simulated concentration to weaken although the general trends are in agreement. At most sites there is a close match between observed and simulated pH but there are discrepancies in observed and simulated Al concentrations at several sites. The close match between observed and simulated under this rigorous test of the model using best available site information and input-output data demonstrates that the model captures the key controls on mean annual surface water chemistry.

At all sites, the improvements in chemistry predicted under the current legislation scenario (Gothenburg Protocol) is clearly greater than for the Oslo Protocol providing quantification of the benefits of the stricter emission controls. At three of the sites, the calculated critical load for acidity using the steady-state water chemistry method and the dynamic model run into the future (2090) with the same ANC target, give a similar load thereby demonstrating consistency between the approaches.

The modelling work undertaken here has not been entirely carried out by the nominated ICP IM National Focal Points but rather has brought together the relevant data holders and modellers with a common aim. This has important implications for resourcing at national and international level.

1 Introduction

The Multi-Pollutant, Multi-Effect Protocol, under the UN ECE Convention on Long Range Transboundary Air Pollution, signed in Gothenburg in 1999, was aimed at reducing atmospheric emissions of sulphur (S), nitrogen (N) and Volatile Organic Compounds (VOCs) to reduce the effects of soil and surface water acidity, eutrophication and ground level ozone. The ecosystem effects of these pollutants and the emission reduction requirements were linked by the calculation of critical loads calculated for sensitive receptors across Europe. For surface waters, critical loads for S and N are defined with respect to acidification as the load of S and N below which significant biologically harmful effects do not occur, according to present knowledge. Critical loads then are calculated to achieve a critical concentration which is defined as the threshold for ecosystem impacts related to biological receptors. In soils this is often taken to be a base cation to aluminium (Al) ratio of 1.0 or in waters an ANC of zero (in the UK) or 20 $\mu eq\ l^{-1}$ (in Norway).

There exists a growing body of evidence to link biological receptors to critical chemical concentrations in surface waters (Ormerod *et al*. 1990) although the relationship for soils is less well identified (Hruška *et al*. 2001). The key consideration in the critical load assessment, however, is that the deposition load is required to lead to the critical chemical concentration at some equilibrium timescale, i.e. when the ecosystem has reached a steady-state with the deposition at the critical load. This could be many hundreds of years into the future, the timescale being dependent on the catchment weathering characteristics, soil characteristics controlling base cation exchange, the amount of historical S and N deposition, the required future reduction in deposition and the timescale over which this will be achieved.

Dynamic models provide the possibility to determine how long it will take to reach the critical chemistry at a given deposition load and to determine the chemistry to be expected at a given timescale in response to a given deposition reduction. They can also be used to determine the load required to meet a chemical criteria within a given timescale. Of these, the first and last relate to the use of models in assessing emission reduction agreements whilst the middle relates to the future use of dynamic model output for calculating new emission reduction agreements. Dynamic models of acidification are already at an advanced state of development and are currently capable of being used to achieve the objectives of the Convention with respect to assessment of the Gothenburg Protocol. Dynamic models capable of predicting soil and surface water eutrophication and changes in heavy metals are less well developed as are biological response models. The acidification models, therefore, act as a demonstration of the importance and capabilities of dynamic models with respect to the objectives of the Convention.

Critical loads assume a steady-state situation and only two cases can be distinguished when comparing them to deposition at a given site (or grid square): (1) deposition is below critical load(s), i.e. does not exceed critical loads, and (2) deposition is greater than critical load(s), i.e. there is critical load exceedance. In the first case there is no (apparent) problem, i.e. no reduction in deposition is deemed necessary. It is possible, however, that although the deposition at one point in time is above the critical load, this may not always have been the case and the ecosystem may still be damaged. In the second there is, by definition, an increased risk of

damage to the ecosystem and, therefore, the deposition should be reduced. A critical load serves as a warning as long as there is exceedance, since it tells that deposition should be reduced. It is often assumed, however, that reducing deposition to (or below) critical loads immediately removes the risk of 'harmful effects', i.e. the chemical parameter (e.g. the surface water ANC), which links the critical load to the effect(s), immediately attains a non-critical ('safe') value and that there is immediate biological recovery as well. But the reaction of soils, especially their solid phase, to changes in deposition is delayed by (finite) buffers, the most important being the soils exchangeable complex represented by cation exchange capacity (CEC). The buffer mechanisms can delay the attainment of a critical chemical parameter and it might take decades or even centuries before an equilibrium (steady state) is reached. These finite buffers are not included in the critical load formulation, since they do not influence the steady state but only the time to reach it. Therefore, dynamic models are needed to estimate the times involved in attaining a certain chemical state in response to deposition scenarios, in addition to the delay before the 'original' or 'acceptable' biological state is reached. The link between critical loads and dynamic models is provided by demonstration that the calculated critical load leads to attainment of the critical chemistry over a very long timescale in the dynamic model. For the further extension of the critical loads concept into dynamic modelling, it is a requirement that this consistency between the approaches is assured.

The calibration of dynamic models at a site requires a range of data describing soils and surface water physical and chemical characteristics together with information describing all chemical inputs and outputs to the system over time; essentially the net uptake of ions to the vegetation, the input of ions from weathering and the input of ions from the atmosphere. Many of the ICP IM sites have the required data for the model application and, in addition, now have many years of observed surface water chemistry against which the performance of the model can be assessed. The role of ICP IM, therefore, in providing the requirements of the Working Group on Effects with dynamic modelling for the revision of the Gothenburg Protocol and potential negotiation of new Protocols is:

(i) To provide for 'best' possible model calibrations using comprehensive and internally consistent data which is often not available at a regional scale.
(ii) To test the capability of the model in capturing observed chemical changes in soils and surface waters in response to observed changes in atmospheric deposition inputs.
(iii) To use these calibrations to assess the model structure and our understanding of the key processes operating to control soil and surface water chemistry.
(iv) To undertake formal model sensitivity analysis using the long-term trend data and observed variance in the 'measured' parameters; and
(v) To provide improved confidence in regional model application within the context of these more detailed site calibrations.

The aim of this report is to demonstrate the utility of the ICP IM data with regard to the overall objectives of the Convention. This is achieved by documenting applications of the MAGIC model (more information in the following chapter) to six catchments in the ICP IM; SE04 (Gårdsjön), NO01 (Birkenes), FI03 (Hietajärvi), DE01 (Forellenbach), GB02 (Afon Hafren) and CZ02 (Lysina). The model is compared with long-term data, used to assess the predicted chemistry under the Gothenburg (Current Legislation) and Oslo Protocols; the consistency with calculated critical loads is assessed; model uncertainty in relation to N dynamics and sea-salt influences is explored.

It is important to stress that the modelling work undertaken for this report has not been entirely carried out by the nominated ICP IM National Focal Points (NFPs) for each country. This is inevitable since the modelling expertise and the data often reside in institutions other than the NFPs. This has caused no problems during this exercise and it is hoped that the dynamic modelling activities in other countries will serve to bring together the relevant scientists with a common aim. There are implications, however, for resourcing these activities if institutes other than the NFPs are required to undertake dynamic modelling work in support of the ICP IM in particular, and the UN ECE Convention in general. The issue of resources must be addressed at national level.

2 The model and data requirement

This report is concerned only with the comparison of observed and simulated surface water chemistry using the MAGIC model. It is clear, however, that the surface water cannot be modelled independently from the soil and in MAGIC the catchment soils are aggregated spatially in line with the run-off observation which aggregate the whole catchment response. Other dynamic models exist which predict changes in soil chemistry at a plot scale (Posch *et al.* 2003a). Surface waters represent the best possibility for dynamic model assessment in relation to the Convention, however, since (i) they are expected to respond much more quickly than soils in response to emission reductions; (ii) time series data exists to demonstrate the capability of the model, unlike soils, and (iii) as already stated, the link between critical concentration and biological receptors is further advanced than for soils (Jenkins *et al.* 2002).

2.1 The MAGIC model

MAGIC (**M**odel of **A**cidification of **G**roundwater **I**n **C**atchments) is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on soils and surface water chemistry (Cosby *et al.* 1985a,b,c, 1986). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in lakes and streams. MAGIC represents the catchment with aggregated, uniform soil compartments (one or two) and a surface water compartment that can be either a lake or a stream. MAGIC consists of (1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO_4 adsorption, cation exchange, dissolution-precipitation-speciation of Al and dissolution-speciation of inorganic and organic carbon, and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering inputs, net uptake in biomass and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change in surface water acidity thus depend both of flux factors and the inherent characteristics of the affected soils.

The soil layers can be arranged vertically or horizontally to represent important vertical or horizontal flowpaths through the soils. If a lake is simulated, seasonal stratification of the lake can be implemented. Time steps are monthly or yearly. Time series inputs to the model include annual or monthly estimates of (1) deposition of ions from the atmosphere (wet plus dry deposition); (2) discharge volumes and flow routing within the catchment; (3) biological production, removal and transformation of ions; (4) internal sources and sinks of ions from weathering or dissolution/precipitation reactions; and (5) climate data. Constant parameters in the model include physical and chemical characteristics of the soils and surface waters, and thermodynamic constants. The model is calibrated using observed values of surface water and soil chemistry for a specific period.

MAGIC has been modified and extended several times from the original version of 1984 (Jenkins *et al*. 2002). In particular, organic acids have been added to the model (version 5; Cosby *et al*. 1995) and most recently N processes have been added (version 7; Cosby *et al*. 2001). The MAGIC model has been extensively applied and tested over a 17 year period at many sites and in many regions around the world (Cosby *et al*. 2001). Overall, the model has proven to be robust, reliable and useful in a variety of scientific and managerial activities.

2.2 List of required data

The data requirement to run MAGIC must be spatially and temporally averaged (or 'lumped') to represent the whole catchment area and the time step of the model (annual or monthly). If physical and chemical data are available at only one point in the catchment or from one point in time, it must be assumed that this is representative of the whole catchment at that time step. Any uncertainty in these data and in the representativeness is incorporated into the model and the prediction must be interpreted accordingly. The minimum data requirement is given below:

Hydrological parameters:
- Annual runoff (m/yr)
- Annual precipitation depth (m/yr)

Soil parameters:
- Soil depth (m)
- Porosity (%)
- Bulk density (kg/m^3)
- CEC (meq/kg)
- SO_4 maximum adsorption capacity (meq/kg)
- SO_4 half-saturation constant (meq/m^3)
- Dissociation constant for aluminium hydroxide solid phase, $KA1(OH)_3$ (log_{10})
- Temperature (annual average) (^{0}C)
- pCO_2 (%)
- Organic acids (mmol C/m^3)
- Dissociation constants for organic acids (pK)
- Nitrification (% of input)

Surface water parameters:
- Retention time (Yr)
- Relative area (%)
- Temperature (annual average) (^{0}C)
- Dissociation constant for aluminium hydroxide solid phase, $KA1(OH)_3$ (log_{10})
- pCO_2 (%)
- Organic acids (mmol C/m^3)
- Dissociation constants for organic acids (pK)
- Nitrification (% of input)

Surface water/soil chemistry in calibration year (i.e. 2001):
- Concentration of major ions (Ca, Mg, Na, K, Al, NH_4, SO_4, Cl, NO_3, F) (meq/m^3)
- Soil exchangeable base cations (Ca, Mg, Na, K) (meq/kg)

Deposition parameters in calibration year (i.e. 2001):

- Concentration of major ions (Ca, Mg, Na, K, NH_4, SO_4, Cl, NO_3, F)
- Time sequence of change in:
  - deposition concentration
  - dry deposition factors for each ion (= total deposition/wet deposition)

The historical sequences of changing deposition of S (Mylona 1993) and N (Simpson *et al*. 1997) are usually derived from estimates made by EMEP. These historical 'trajectories' at the scale of the EMEP grid are usually modified at a site or regional scale to incorporate more detailed measurements or estimates, particularly in more recent years. Further updated deposition histories for the EMEP grid are currently being derived by the CCE/CIAM (Posch, *pers. comm.*).

More detailed data is desirable to describe:

- dry deposition flux
- uptake to plant biomass in soil and water
- in-lake processes (stratification, sedimentation, etc.)
- forest growth history

These data, if available, can improve the model performance against observations and serve to increase confidence in model predictions. In addition to the data required to parameterise the model, information is also required to enable model calibration.

2.3 Model calibration

The calibration of MAGIC is a sequential process whereby firstly the input and output of those ions assumed to act conservatively in the catchment are balanced (usually only Cl); next, the anion concentrations in surface waters are matched by adjusting catchment net retention (of N) and soil adsorption (of S) if appropriate. Thirdly, the base cation concentration in the stream and on the soil solid phase (expressed as a percentage of cation exchange capacity) are matched by adjusting the cation exchange selectivity coefficients and the base cation weathering rates. In practice, however, the pre-industrial soil base saturation is estimated and adjusted and the model calculates the four cation exchange selectivity coefficients. Finally, surface water pH and Al concentrations are matched by adjusting the Al solubility coefficient.

The first step is achieved through comparison of the present day deposition concentration of Cl, the rainfall amount (which together provide the input flux), the surface water concentration of Cl and the runoff (which together provide the output flux). In most cases the input is less than the output and it is assumed that the extra Cl is deposited as sea-salt that is not represented by the wet deposition concentration. This extra sea-salt Cl is added as a neutral salt by also adding base cations and SO_4 in their sea-salt ratio to the deposition flux.

Observed inputs of N are usually much higher than observed N concentrations in surface waters. Indeed, NH_4 concentrations are usually very low. For calibration, nitrification of NH_4 is usually assumed to be 100% at each time step and the net catchment retention required to match the observed nitrate (NO_3) concentration in the surface water is calculated. This percentage retention is assumed to be constant throughout the model simulation. For SO_4, if surface water data is available for only one point in time the adsorption parameters (Maximum adsorption capacity = E_{mx} and Half-saturation constant = C) if required, must be estimated from soils data. For regions with geologically 'young' soils, SO_4 adsorption is generally

considered negligible (Rochelle *et al*. 1987). For the applications considered here, however, long time-series provide the opportunity for calibrating C and E_{mx} to match the observed trend in surface water SO_4 given an observed trend in SO_4 deposition.

The base cation calibration follows an iterative process whereby the base cation selectivity coefficients are set, values are chosen for base cation weathering, the model is run from some background, pre-acidification condition, the simulated values of base cations in soil and surface waters are compared with observed. This process is repeated, adjusting the selectivity coefficients and weathering rates until the observed target concentrations are achieved. If time-series data are available further adjustment may be undertaken to match trends. This calibration procedure can be undertaken automatically using an appropriate numerical optimisation procedure.

2.4 Site descriptions

The location of the sites modelled here and those where suitable data currently exist on the ICP IM database is given in Figure 1. The six ICP IM sites selected for dynamic modelling receive varying loads of S and N deposition and have very different catchment characteristics (Table 1). In addition, the agreed reductions in N and S in response to agreed protocols vary between the sites (Table 2) depending on their location. The sites, therefore, provide a wide range of possible future responses to the agreed emission reduction scenarios.

Birkenes (NO01)

The Birkenes calibrated catchment is located in Vest-Agder county in Southern Norway about 20 km from the coastline. The catchment area is 0.41 km^2 and the elevation 200-300 m a.s.l. The catchment is mainly vegetated by mature 80-year old Norway spruce (*Picea abies*) and has an undergrowth of mosses, blueberry and fern. Mineral soils have developed in a shallow layer of glacial till on granitic bedrock. Mineral soil types are acid brown earths and podzols. Peaty deposits have developed at poorly drained deposits in the catchment. On the slopes, well drained thin organic layers on gravel or bedrock are common. The catchment is drained by three small second order streams, which converge about 150 m above the V-notch weir.

Hietajärvi (FI03)

The 464 ha Hietajärvi (63^0 10'N, 30^0 43'E) monitoring area is located in Eastern Finland in the province of North Karelia. The monitoring area is part of Patvinsuo National Park, which was established 1982. It consists of two catchment areas with shallow, oligotrophic lakes. Lakes and ponds account for 23 % of the area and the stream drains from the largest lake Iso Hietajärvi. The Hietajärvi area lies in a transition belt between two vegetation zones – the middle boreal and southern boreal. The forests are mainly mature or old, but the northern and eastern parts have young cultivated forest stands. Scots pine (*Pinus sylvestris*) is the dominant tree species with Norway spruce (*Picea abies*), birch (*Betula spp.*) and aspen (*Populus tremula*) occurring among the pine (Bergström *et al.* 1995, Tuominen 2001). The relief of the Hietajärvi area is rather low (49 m), elevation is between 165 and 214 m a.s.l. Long term mean annual temperature is 2.0^0C, precipitation is 592 mm. The dominant rock types are Archean acidic granitoids. Weathered bedrock (mostly porphyritic types) is observed in a few places. The Hietajärvi area is supraaquatic; however, during the period when the ice was retreating, the meltwater washed the uppermost layers of loose till, removing the finer material. Over a third of the area is covered by fibric histosols, with the remaining area being mainly comprising haplic and ferric podzols.

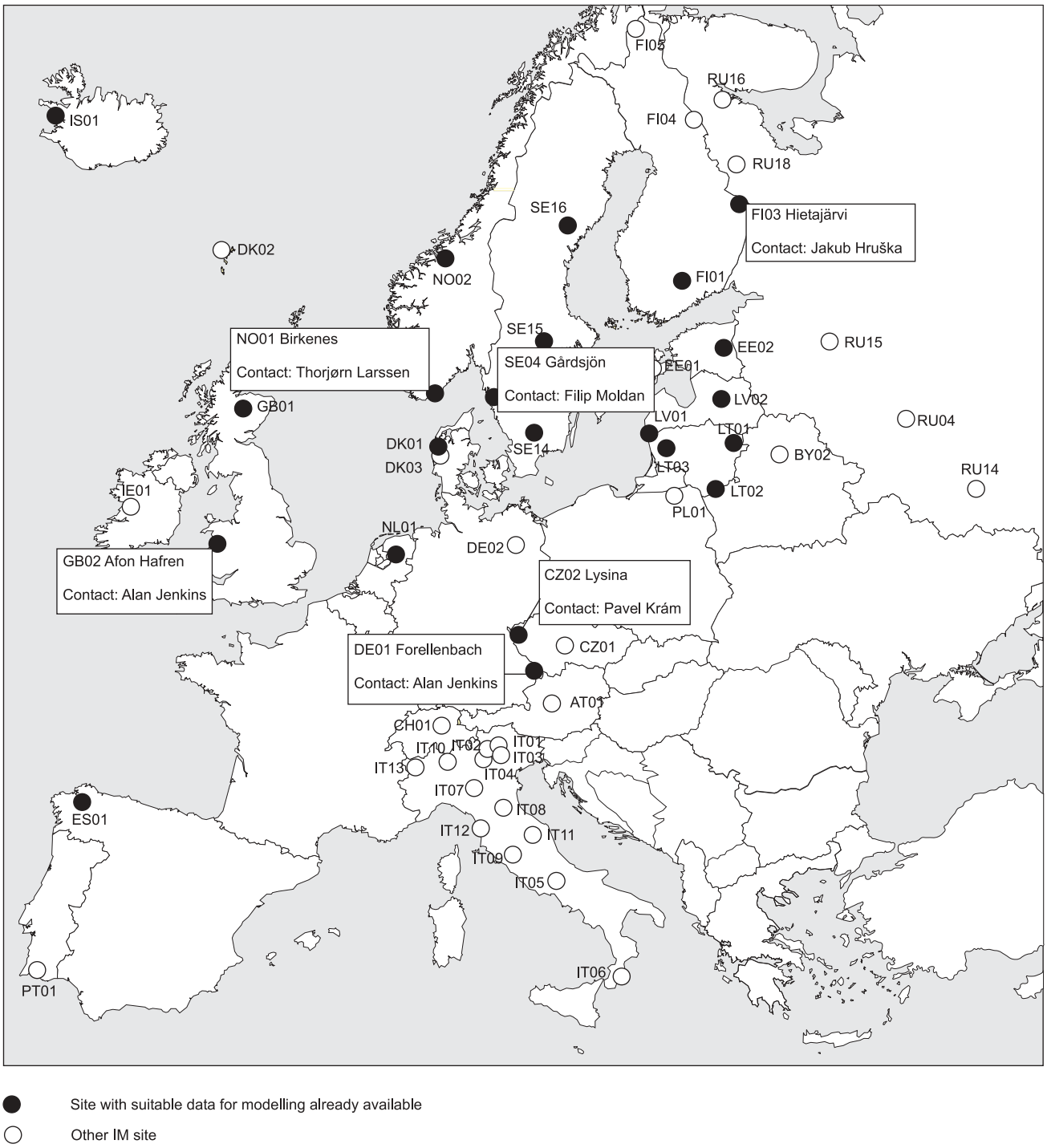

***Figure 1**. The location of the ICP IM sites. Those modelled here are indicated by boxes. Only some of the suitable sites have been modelled so far, additional sites could be included in the future. Contact person is the person who applied the model. Those sites where data exists (and has been reported to the ICP IM database) to apply a dynamic model are shown as solid circles and all other sites as open circles. Data suitable for dynamic modelling may be available at other sites but these are not currently held on the ICP IM database and may be held by National Institutes other than the ICP IM National Focal Points.*

Forellenbach (DE01)

The 69 ha Forellenbach (48^0 56'N, 13^0 25'E) monitoring area is located in 'National Park Bayerischer Wald' in Bavaria close to the border of Czech Republic. Geologically, the area is characterised by very old rocks comprising carboniferous granite and gneiss. The soils mostly consist of dystric cambisols (58%) on solifluction deposits, dystric gleysols, gleyic cambisols and histosols (30%). The relief of the Forellenbach area is 505 m with elevation range between 787 and 1292 m a.s.l. Long term mean annual temperature is between 6.5^{0}C (780 m a.s.l.) and 3.5^{0}C (1290 m a.s.l.) and mean annual precipitation increases with altitude from 1350 mm (780 m a.s.l.) to 1900 mm (1290 (m a.s.l.). The site is 95% covered with forest. In 1990, Norway spruce was the dominant species (69%), 31% of the forest was covered with deciduous species predominantly beech (*Fagus sylvatica*). The forest age classes are: <70 years 27%, 71-110 years 63%, >110 years 10%. In 2001 the coverage of Norway spruce decreased by about half to 34% (analysis of CIR-pictures) caused by bark beetle attack killing Norway spruce older than 70 years. Volume stock of spruce timber over bark was reduced in the same order from 401 m^3 ha^{-1} (1990) to 207 m^3 ha^{-1} (2001). In contrast, volume stock of beech increased from 93 m^3 ha^{-1} (1990) to 128 m^3 ha^{-1} (2001).

Lysina (CZ02)

The 27 ha Lysina catchment (50^0 03'N, 12^0 40'E) is situated in the western part of the Czech Republic in the mountain region of the Slavkov Forest. The region is generally forested with Norway spruce. Catchment altitude is between 829-949 m a.s.l. with mean slope of 11.5%. Mean annual temperature is 5^{0}C, man annual precipitation 950 mm. The bedrock is coarse-grained leucogranite with only trace amounts of biotite. The catchment was not glaciated and is overlain by soil derived from residuum. The dominant soil is podzolic brown forest earth. Much of the catchment (70%) is covered by managed, even-aged stands of Norway spruce. The remaining 30% is covered by very young spruce forest and grass, mainly small reed *(Calamagrostis villosa)*. The spruce stands average 50 years in age.

Afon Hafren (GB02)

The Afon Hafren lies in the Cambrian Mountains of mid-Wales. The catchment area is 358 ha and from its confluence with the Afon Hore forms the headwaters of the River Severn. The catchment rises from 355 m at the sampling station to 690 m at Blaenhafren. Podzols cover approximately 60% of the catchment and organic peaty soils comprise the remaining area. The underlying geology consists of Ordovician grits and Silurian mudstones and shales. 50% of the catchment is planted with conifers, primarily Sitka and Norway spruce and forms part of the larger Hafren

Table 1. Descriptions of sites used for dynamic model applications.

Code	Name	Coordinates	Total area (ha)	Lake area (ha)	Forest area (%)	Forest age (a)	Dominant vegetation
DE01	Forellenbach	48°56'N 13°25'E	68.8	0	95	90	Norway spruce
CZ02	Lysina	50°03'N 12°40'E	27.3	0	100	50	Norway spruce
FI03	Hietajärvi	63°10'N 30°43'E	464.0	23	42	>100	Scots pine
GB02	Afon Hafren	52°29'N 03°41'W	358.0	0	51	<50	Sitka/Norway spruce
NO01	Birkenes	58°23'N 08°15'E	41.6	0	90	80	Norway spruce
SE04	Gårdsjön	58°03'N 12°01'E	3.7	0	100	80	Norway spruce

Forest; planting took place primarily between 1948-1950 and 1963-1964. There has been some thinning and windblow, with removal of windblown trees and to 1992 about 5% of the catchment consisted of recently felled forest. Moorland grasses and *Calluna* occupy the remainder of the catchment and are utilised for rough grazing.

Gårdsjön (SE04)

The 3.7 ha Gårdsjön catchment (58^0 03'N 12^0 0l'E) is located in southwestern Sweden, about 50 km north of Gothenburg. Altitude in the catchment ranges from 115 to 135 m. Bedrock is gneiss and granodiorite partly overlain by glacial till upon which podsols, and in the valley bottom histosols, have developed. The vegetation is predominantly mature mixed forest of Norway spruce, birch and Scots pine. The ground vegetation consists primarily of blueberry (*Vaccinium sp.*), grass (mainly *Deschampsia flexuosa*), abundant mosses (mainly *Dicranum maius*) and lichens *(Hypogymnia physodes, Lepraria incana*). The site was instrumented in 1979 and has been continuously operated by IVL Swedish Environmental Research Institute since 1980 (Andersson and Olsson 1985).

Table 2. Scale factors used for 2010 deposition relative to deposition in 1990. The first scenario is the Current Legislation (CLE) and the second is the Oslo Protocol. The nitrogen values are set equal to 1990 for the Oslo Protocol as nitrogen was not included. The CLE scenario approximates the Gothenburg Protocol to 2010 but also includes agreement under the National Emissions Ceilings Directive and the Large Combustion Plants Directive.

	CLE			2nd S Protocol (Oslo)		
	SO_4	NO_3	NH_4	SO_4	NO_3	NH_4
Birkenes	0.33	0.56	0.88	0.47	1	1
Hietajärvi	0.43	0.59	0.85	0.53	1	1
Gårdsjön	0.37	0.59	0.82	0.54	1	1
Forellenbach	0.30	0.55	0.93	0.50	1	1
Lysina	0.18	0.53	0.96	0.37	1	1
Afon Hafren	0.21	0.54	0.91	0.36	1	1

EMEP i,j coordinates used for the sites above:

Birkenes	7,20; 17,19; 16,20; 16,19 (combination of the four south Norwegian grids)
Hietajärvi	20,28
Gårdsjön	9,20; 19,21; 18,21 (combination of the three grids around approximate location of Gårdsjön)
Forellenbach	24,16
Lysina	23,17
Afon Hafren	6,13

2.5 Site applications

The model applications documented here utilise best available soils and water chemistry data held on the ICP IM database in Helsinki. Where possible/necessary, this is augmented by additional data available for each site more fully described elsewhere; Birkenes (Larssen *et al.* 2002), Lysina (Krám *et al*. 1997), Afon Hafren (Jenkins *et al*. 1997), Hietajärvi and Forellenbach (Forsius *et al*. 1998) and Gårdsjön (Moldan *et al*. 1995, Andersson and Olsson 1985). The historical S deposition trajectories (since pre-industrial time) are based on those developed by EMEP (Mylona 1993). The full record of annual deposition chemistry is used to drive the model to present day for comparison with observed runoff chemistry. Forecasts all use the EMEP deposition for the relevant grid square in which the site is located (Table 2). The key soil and water physical and chemical fixed and optimised parameters at each site are given in Table 3.

For the model calibration, historical S and N deposition was derived from EMEP scale assessments (Mylona 1993, Simpson *et al.* 1997). These curves were scaled to match the deposition measured at the sites at the start of monitoring (Note that this start year varies at each site). Thereafter, the measured/estimated annual deposition was used as input to the model until present day (2000). This has enabled the comparison of simulated and observed data.

Beyond 2000, two deposition reduction scenarios were utilised: the current legislation plans and the Oslo Protocol. Both of these scenarios were supplied from the CIAM/CCE (Posch *et al*., 2003b). The Oslo Protocol scenario is the predicted change in S deposition (no change in N) to 2010 with the implementation of the Second Sulphur Protocol. The Current Legislation scenario approximates the Gothenburg Protocol to 2010 but also includes agreement under the National Emissions Ceilings Directive and the Large Combustion Plants Directive.

3 Results

Birkenes (NO01)

At NO01 the model captures well the decreasing trends of both non-marine SO_4 and Ca+Mg concentrations (Figure 2) since the mid 1970s. Non-marine SO_4 concentration has reduced significantly from c. 140 µeq l^{-1} in the early 1970s to c. 60 µeq l^{-1} in 1998-2000 as a result of a c. 60% decrease in the S deposition. The trend in Al concentration is more noisy and less clear than for SO_4 and the non-marine base cations. In individual years the model results deviate from the observed, but the general trend captures that of the observed concentrations. Similarly, the increasing trend in ANC is relatively well captured in the model simulation, although there are large deviations for individual years. The especially large deviations for some years for the Al concentration and ANC are related to the variation in the frequency and magnitude of winter storms. Since the Birkenes catchment is located close to the sea, the deposition is heavily influenced by sea salts. An example of such sea salt influence is seen for the year 1993, where the model predicts a higher annual average Al concentration and lower annual average ANC than observed. The high sea salt deposition given as input to the model for this particular year gave a peak in modelled Al concentration and a dip in ANC. The observations show a more damped response. The discrepancy can be explained by the use of annual average data in the modelling and the fact the model was run with calendar year time steps. The long term perspective of the modelling exercise justifies the use of annual average data since the long term future trends are the focus of the exercise.

The modelled soil base saturation (Figure 9) has decreased considerably over the last 150 years (from c. 23% to c. 10% today). Only a small increase is predicted for the next decades, but nevertheless the base saturation is beginning to replenish.

The prediction to 2020 shows a further improvement in ANC, albeit rather slowly since SO_4 concentration is predicted to decline only a little further than present, even under the CLE emission reduction scenario. Nevertheless, there is predicted to be clear benefit in implementing the CLE scenario as ANC nears zero by 2020, compared to the Oslo Protocol where ANC remains well below zero. At this site further reductions in acid deposition are necessary in order to achieve a water quality which is acceptable for a reproducing stock of brown trout.

The critical load for Birkenes calculated using the SSWC model is 27 meq m^{-2} yr^{-1} (acidity). In comparison, running MAGIC forward to achieve the same target ANC in 2090 gives a critical load of 28 meq m^{-2} yr^{-1}. Clearly, the static critical load is consistent with the dynamic model output at Birkenes.

Hietajärvi (FI03)

At FI03, there has been a significant decrease in SO_4 deposition since 1989 and this is reflected in a rapid decline in surface water SO_4 concentration (Figure 3). The model is able to reproduce this pattern well although the slight under-prediction in the period 1996-1999 indicates that there may be some process which is maintaining SO_4 concentration above that expected from the changes in deposition alone. This may reflect soil S adsorption or may also reflect inaccurate deposition

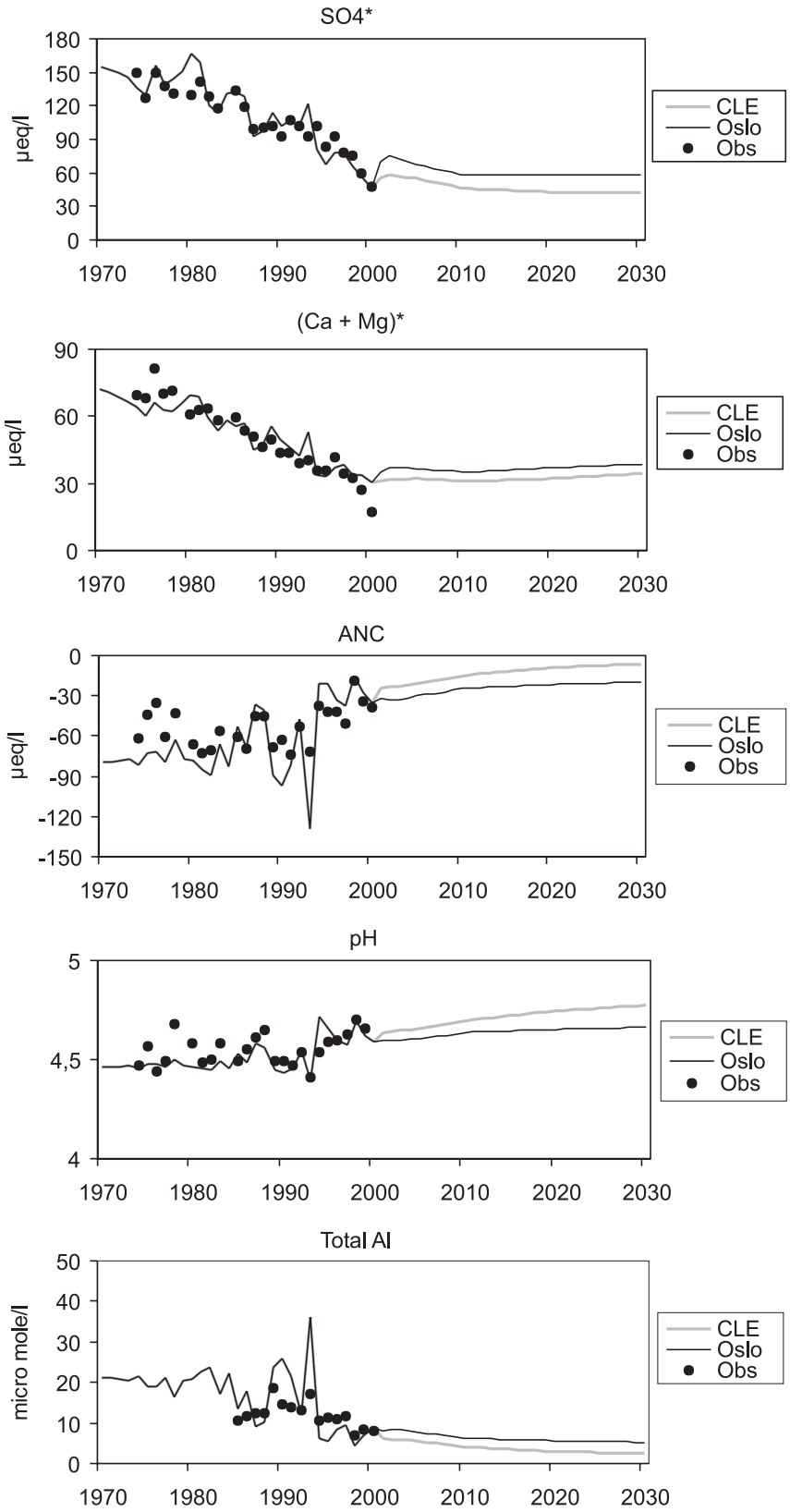

***Figure 2**. Simulated and observed surface water chemistry and predictions under the Current Legislation (CLE) and Oslo Protocol scenarios at Birkenes.*

estimates. The slight increase in SO_4 concentration beyond 2000 to 2005 reflects the fact that the deposition as measured in 1999 has already dropped to that predicted for 2010 under the CLE and Oslo Protocol and the forecast assumes a linear decline to those values in 2010.

The model has considerable difficulty in matching the observed concentration of excess base cations which are relatively constant through the period of record. Given the rapid decline in SO_4, this leads to the observation of a rapid increase in ANC. Again, the model does not match such a rapid increase in ANC. In many respects, however, the observed response is unusual; the lack of trend (downwards) in the excess base cations implies that as the SO_4 changes, all of the response is accounted for by increased ANC (i.e. an F-factor of almost zero) and there is no change in the rate of ion exchange from the soil. At such a well buffered site with ANC around 90 µeq l^{-1}, this is unusual as it implies that the base cation concentration represents a constant flux from weathering alone. The model can only approximate this behaviour by forcing the soils to maintain their base cation status through time (high organic acids and very high $Al(OH)_3$ solubility constant). The calibrated ion-exchange selectivity coefficients are consequently extremely low and fall well outside of those measured in laboratory studies (Table 3). This clearly requires further analysis of both the data used for parameterization and the model structure.

Surface water pH at this site is consistently between 6.5 and 7.0 throughout the observation and simulation period and total Al concentrations are always below 1.0 µmol l^{-1} and so are not shown.

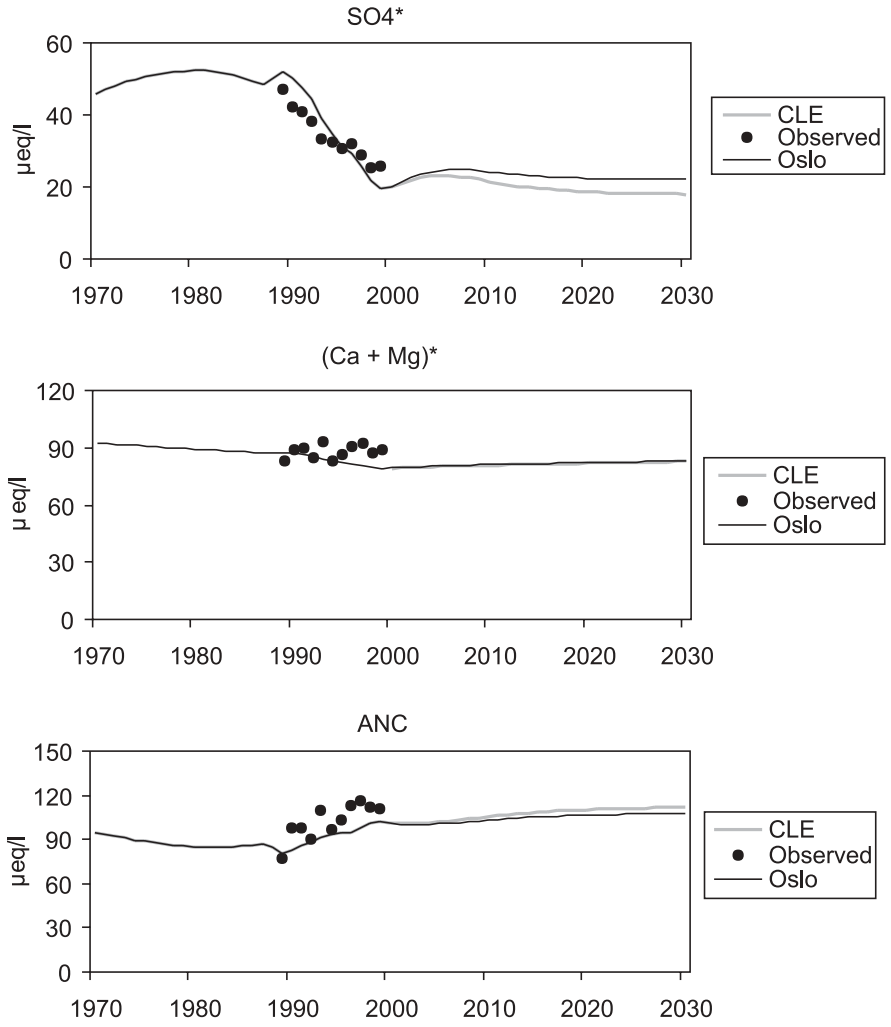

***Figure 3**. Simulated and observed surface water chemistry and predictions under the Current Legislation (CLE) and Oslo Protocol scenarios at Hietajärvi.*

Forellenbach (DE01)

At DE01 the model matches the general trend in stream SO_4 over the nine years of observed data but does not reflect the annual variation observed (Figure 4). This is because of the high level of soil SO_4 adsorption required in the model to match observed inputs to outputs. Despite an observed decrease in S deposition since 1990, therefore, SO_4 concentrations have remained relatively stable due to the large pool of S stored within the soils which is released slowly relative to any decline in S deposition. As a result, the model is also unable to match the annual variation in excess base cations and ANC although it captures the mean downward trend over the observation period. The decline in ANC over the period 1990-2000 must reflect the constant SO_4 concentration but slightly reduced excess base cations, implying a continued decline in soil base saturation.

Predictions to 2020 show that ANC is stabilized under the CLE scenario although continues to decline under the Oslo Protocol. This implies that the critical load at this site is very close to the deposition under the CLE.

The critical load for acidity for this site calculated using the SSWC method is 160 meq m^{-2} yr^{-1}. In comparison, running MAGIC forward in time to achieve the same target ANC in 2090 gives a load of 140 meq m^{-2} yr^{-1}. Over a longer time period, the required load would increase to match the steady state calculation and the dynamic model output is entirely consistent with the steady state critical load model. Note that at this site, the deposition of S is already below the calculated critical load.

Lysina (CZ02)

The MAGIC simulated non-marine SO_4, base cations, pH and ANC since 1970 (Figure 5) shows a peak of acidification in the early 1980s. From then until present, the ANC has recovered significantly in response to a large decrease in SO_4 concentration (c. 600 µeq l^{-1} to c. 200 µeq l^{-1}). The model predictions match the observation extremely well. This model application is fully described in Hruška *et al.* (2002). Lysina is a typical catchment where historical depletion of base cations from the soil leads to chronic acidification as characterized by pH decline and Al mobilisation (Figure 5). Pre-industrial exchangeable base cations estimated as c. 7000 meq m^{-2} declined to c. 2500 meq m^{-2} in early 1980s when S deposition peaked. Despite the large decline of S deposition during the 1990s, the soil base cation pool has declined further to 1600 meq m^{-2} in 2000. The MAGIC forecast estimates a slight increase to 1745 meq m^{-2} in 2030 under the Oslo protocol scenario. Under the CLE scenario, a more pronounced increased is expected and the soil base cation pool increases to ca. 1900 meq m^{-2} in 2030.

The modelled historical pH of 5.5 shows the expected susceptibility of granitic catchments to anthropogenic acid loading. High organic acid concentrations produced low streamwater pH prior to the onset of acidic deposition. As a result of S deposition and base cation depletion, pH declined to a minimum annual average of 3.87 during the 1980s. After a decade of declining deposition, the measured and modelled pH was 4.07 in 2000. Under the Oslo protocol scenario, modelled pH rises to 4.2 in 2010 and then slowly to 4.25 in 2030 (Figure 5). Under the CLE scenario pH is predicted to recover to 4.4 in 2030.

Total Al concentrations in the MAGIC model are controlled by $Al(OH)_3$ solubility. The $Al(OH)_3$ solubility constant for Lysina was optimized using measured data between 1990 and 2000. Using fitted $pKAl(OH)_3$ = 7.1 (Table 3), this satisfactorily produced the measured Al and pH. Modelled total Al peaked during the 1980s at an extremely high level of 82 µmol l^{-1}. Measured data showed a decline of 38% during the 1990s (from 68 µmol l^{-1} in 1992 to 42 µmol l^{-1} in 2000, Figure 5). The MAGIC forecast estimated a further significant decline of total Al to 22 µmol l^{-1} in 2010 under

Table 3. Selected parameter values for the MAGIC model calibration at the catchments.

	Units	Lysina	Birkenes	Afon Hafren	Hietajärvi	Forellenbach	Gårdsjön
Fixed parameters							
Discharge, annual	m	0.432	1.15	1.62	0.34	0.87	0.47
Precipitation, annual	m	0.953	1.49	2.14	0.58	1.2	1.1
Soil depth	m	0.90	0.4	0.88	0.65	0.95	0.53
Bulk density	kg m^{-3}	530	773	1133	1000	999	730
CEC	meq kg^{-1}	59	106.8	70	4	57	79
SO_4 adsorption half saturation	meq m^{-3}	500	100	100	100	168	400
SO_4 maximum adsorption capacity	meq kg^{-1}	3	0.1	0.1	0.5	11.5	2.5
pCO_2 soil	atm	0.022	0.33	0.66	0.66	0.66	0.4
pCO_2 stream	atm	0.0011	0.033	0.066	0.07	0.066	0.1
Temperature, soil	°C	5	5	7	4	7	8
Temperature, stream	°C	5	5	7	4	7	8
pK_1 of organic acids, soil	-log 10	2.5	3.0	2.5	2.5	2.5	3.0
pK_1 of organic acids, stream	-log 10	2.5	3.0	2.5	2.5	2.5	3.0
pK_2 of organic acids, soil	-log 10	4.4	4.5	4.0	4.0	4.0	4.5
pK_2 of organic acids, stream	-log 10	4.4	4.5	4.0	4.0	4.0	4.5
pK_3 of organic acids, soil	-log 10	6.7	6.5	5.8	5.8	5.8	6.5
pK_3 of organic acids, stream	-log 10	6.7	6.5	5.8	5.8	5.8	6.5
Organic acids , soil	mmol m^{-3}	110	65	63	250	50	79
Organic acids, stream	mmol m^{-3}	59	10	10	5	5	38
Ca saturation	% of CEC	3.7	3.9	2.9	35.0	1.3	8.5
Mg saturation	% of CEC	0.8	2.1	0.5	7.5	0.7	3.6
Na saturation	% of CEC	0.4	1.1	1.2	3.0	0.5	1.8
K saturation	% of CEC	1.9	2.8	0.6	6.4	1.6	2.4
Total base saturation	% of CEC	6.8	9.9	5.2	51.9	4.1	16.3
Vegetation uptake Ca	meq m^{-2}	12.5	16.6	15.2	6.9	0.0	13
Vegetation uptake Mg	meq m^{-2}	3.8	3.8	4.7	1.5	0.0	4.6
Vegetation uptake Na	meq m^{-2}	0.1	0.0	1.2	0.0	0.0	0.5
Vegetation uptake K	meq m^{-2}	2.3	7.3	5.8	1.6	0.0	3.5
Optimized parameters							
$Al(OH)_3$ solubility constant, soil	log 10	7.7	7.8	9.01	11.0	9.0	8.6
$Al(OH)_3$ solubility constant, stream	log 10	7.1	8.6	10.0	9.0	8.0	7.6
Weathering Ca	meq m^{-2}	29	57	50	24	76	12
Weathering Mg	meq m^{-2}	10	8	26	9	12	18
Weathering Na	meq m^{-2}	22	9	6	13	54	3
Weathering K	meq m^{-2}	4	4	30	4	2	1
Weathering of $\sum(Ca + Mg + K + Na)$	meq m^{-2}	65	78	112	50	144	34
Weathering F	meq m^{-2}	5	0	0	0	0	0
Selectivity coeff. Al-Ca	log	0.78	-0.41	-0.09	-4.97	7.30	-2.19
Selectivity coeff. Al-Mg	log	1.08	-0.28	2.51	-4.13	6.00	-0.004
Selectivity coeff. Al-Na	log	-0.48	-1.24	-0.77	-4.84	1.50	-0.91
Selectivity coeff. Al-K	log	-4.21	-7.34	-4.27	-7.79	-2.44	-5.43
Ca saturation (pre-industrial)	%	16	7.7	7.4	42.3	4.8	11.34
Mg saturation (pre-industrial)	%	5	4.8	1.7	8.4	2.5	8.0
Na saturation (pre-industrial)	%	1	1.6	1.8	3.0	1.3	3.1
K saturation (pre-industrial)	%	2.7	3	1.5	8.5	1.9	2.8
Total base saturation (pre-industrial)	%	24.7	17.1	12.4	62.5	10.5	25.2

the Oslo protocol scenario. Thereafter, Al will stay around 20 µmol l^{-1} for an additional two decades. Under the CLE scenario, total Al will decrease to 15 µmol l^{-1} in 2030. Under both scenarios, pH and Al will stay at unacceptable limits for survival of fish populations (Gensemer and Playle 1999).

Changes in ANC are driven dominantly by changes in Al, H^+ and $RCOO^-$ concentrations. Quite high historical ANC (128 µeq l^{-1}) was the result of high $RCOO^-$ concentration (ANC = $([RCOO^-]-([Al^{n+}]+[H^+]))$ despite low estimated historical pH (5.5) in the middle of the 19th century. Since the 1950s, as Al and H^+ increased while $RCOO^-$ decreased, ANC declined sharply. A minimum ANC was reached during the 1980s (-240 µeq l^{-1}). During the recovery phase in the 1990s, ANC increased sharply to -52 µeq l^{-1} in 1999. As a result of predicted Al, H^+ and $RCOO^-$ dynamics, ANC will rise to c. 0 µeq l^{-1} in 2010 and reach slightly positive values for 2030 under the Oslo protocol scenario. Under the CLE scenario, ANC is predicted to recover further to c.35 µeq l^{-1} by 2030.

Afon Hafren (GB02)

At GB02 the model successfully captures the declining trend observed in streamwater SO_4 concentrations since 1988 (Figure 6) and the annual variation is also closely matched. The decreasing trend in SO_4 is accompanied by a small decline in excess base cations over the same period and, as a result, there is no observed change in ANC which is very variable over the period of observation. These characteristics are well reproduced by the model although the trend of decreased excess base cation in the model is partly offset by increased sea-salt inputs through the period. The large variations in annual sea-salt inputs is also mainly responsible for the large variability in ANC. This causes some mis-match between observed and predicted ANC at any given year but the variance in both observed and predicted values are similar. Similar annual variation is observed in pH which the model does not capture although the constant mean value through the observation period is matched. The model under-predicts total Al concentration (Figure 6).

Beyond 2000, the SO_4 concentration is predicted to decline yet further in response to the CLE scenario with a levelling off of excess base cation concentration and so a pronounced increase in ANC to 2020. The improvement with respect to the CLE beyond the Oslo Protocol is clearly shown (Figure 6). Calculated critical loads for acidity for this site are 51 meq m^{-2} yr^{-1} and 75 meq m^{-2} yr^{-1} for the SSWC and dynamic model in 2090, respectively. The discrepancy between the two methods is related to the assumptions made in the dynamic model regarding the future forest rotation. Nevertheless, the critical load calculated by both methods is achieved under the CLE scenario and the ANC increases above the critical concentration.

Gårdsjön (SE04)

At Gårdsjön the major decline in observed non-marine SO_4 concentration since the early 1980s to 2000 is closely matched by the model (Figure 7). Into the future, under the CLE scenario, the model predicts a small increase in SO_4 as a result of sea-salt inputs which for the last few years have been lower than the long-term average. This effectively pushed the modeled SO_4 concentration down further than would be expected from the decline in SO_4 deposition alone. The Oslo protocol scenario resulted in a clear increase in SO_4 concentration in the stream after 2002 and beyond. This is because the actual measured deposition of S at the site in the years 2001-2002 was already below the expected outcome of the Oslo protocol predicted for 2010. The Oslo protocol scenario therefore leads to an increase in S deposition. After 2002, the sea-salt deposition in the model increases slightly back to the long term average.

In response to the decline in SO_4, the non-marine Ca + Mg has also declined although not on the same slope. This has effected a dramatic increase in ANC of c. 200 µeq l^{-1} which again is well simulated by the model (Figure 7). Part of this increase, however, is again driven by low sea-salt inputs at the end of the 1990s and so the model prediction beyond 2000, assuming the mean sea-salt input, is for a slower recovery. The CLE deposition scenario resulted in a markedly larger future ANC increase, which in 2030 is about 40 $µeq^{-1}$ higher than under the Oslo protocol scenario.

The increasing pH trend is well matched by the model and is predicted to continue into the future under the Gothenburg Protocol scenario as opposed to the Oslo protocol scenario under which the pH stops increasing after year 2000 and remains stable. The simulation of total Al is less good, however, and the model over-predicts the decline in Al concentration. This raises questions over both the model representation of Al processes and the reliabilility of the observed data.

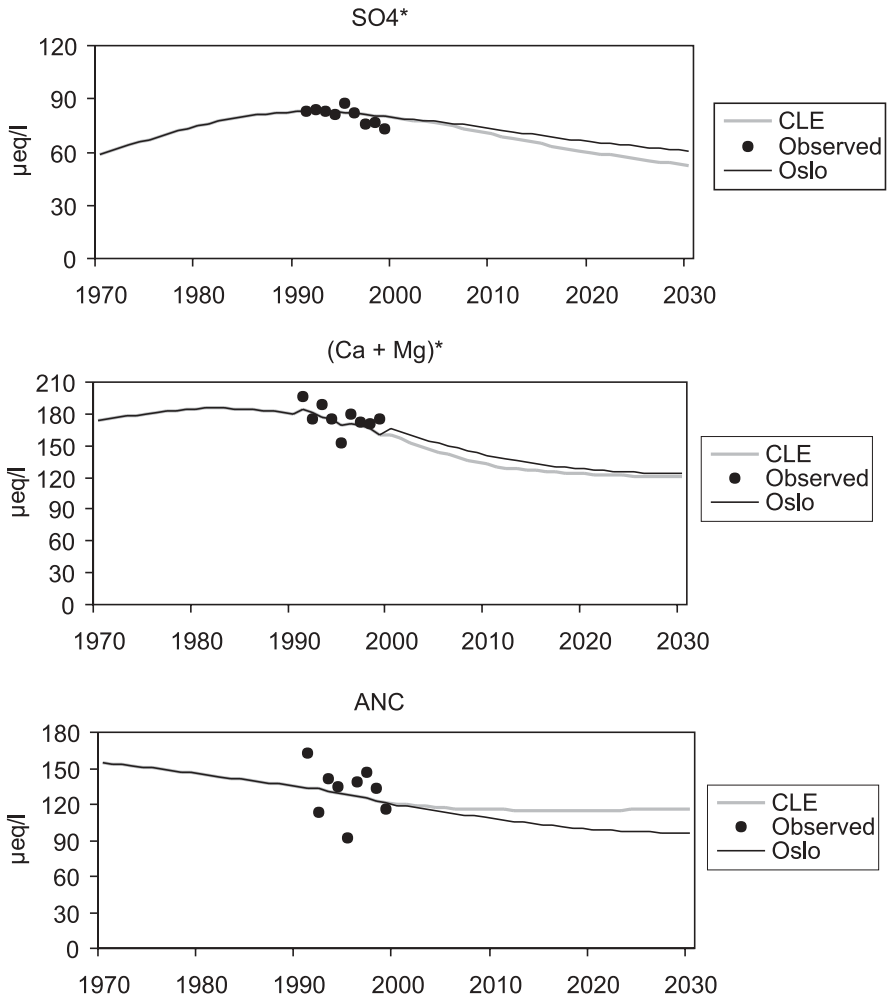

***Figure 4**. Simulated and observed surface water chemistry and predictions under the Current Legislation (CLE) and Oslo Protocol scenarios at Forellenbach.*

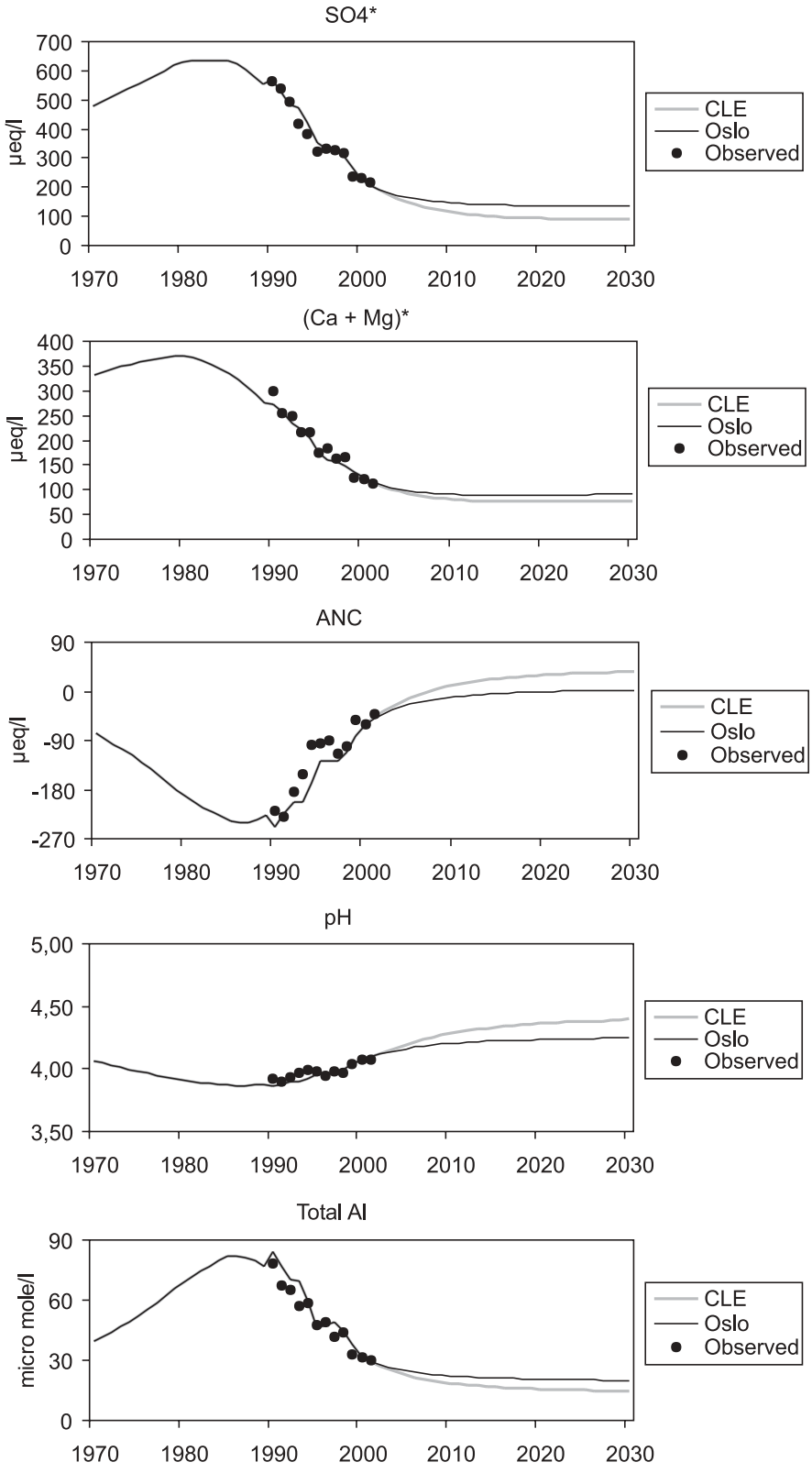

***Figure 5**. Simulated and observed surface water chemistry and predictions under the Current Legislation and Oslo Protocol scenarios at Lysina.*

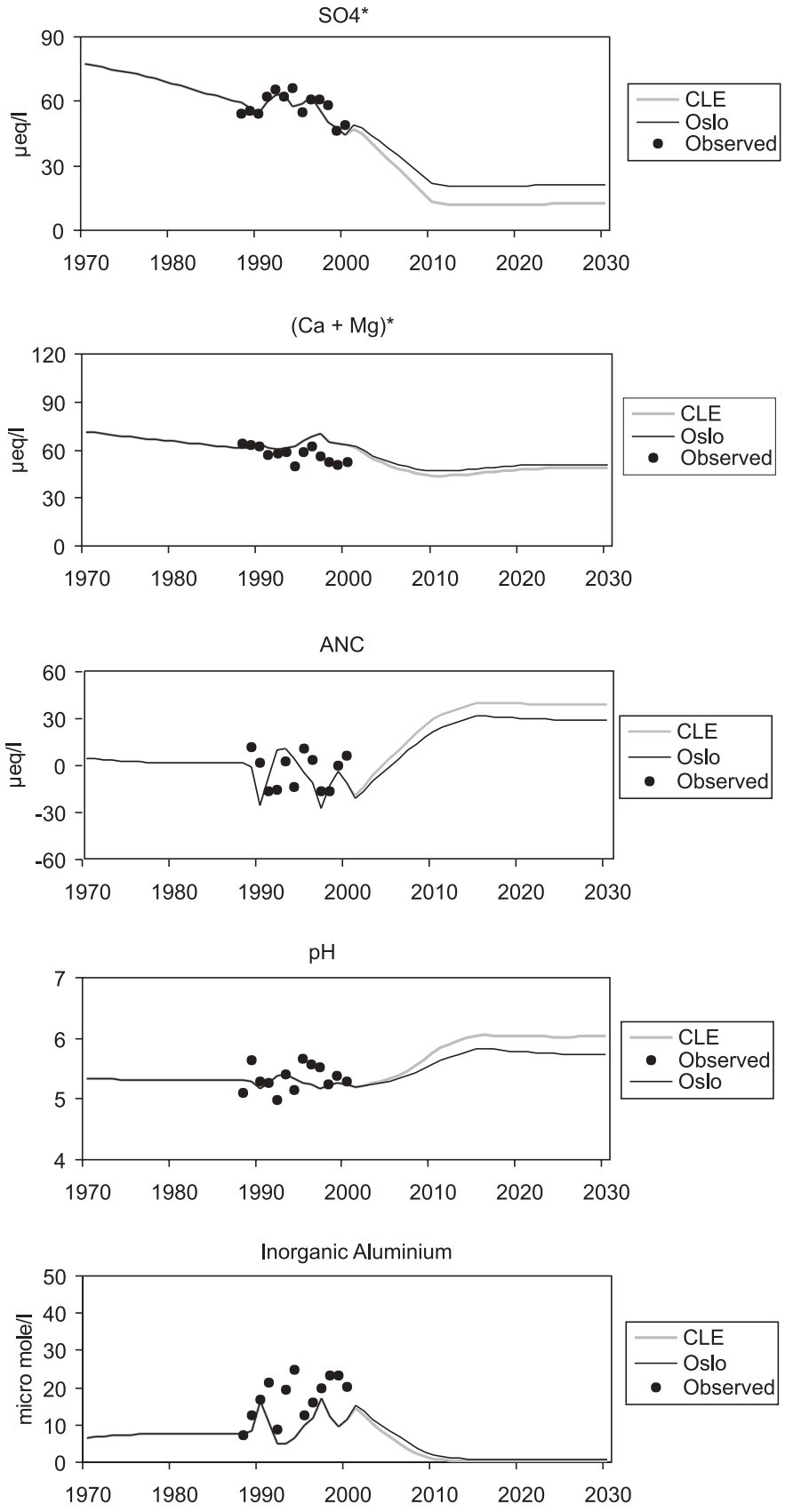

***Figure 6**. Simulated and observed surface water chemistry and predictions under the Current Legislation (CLE) and Oslo Protocol scenarios at Afon Hafren.*

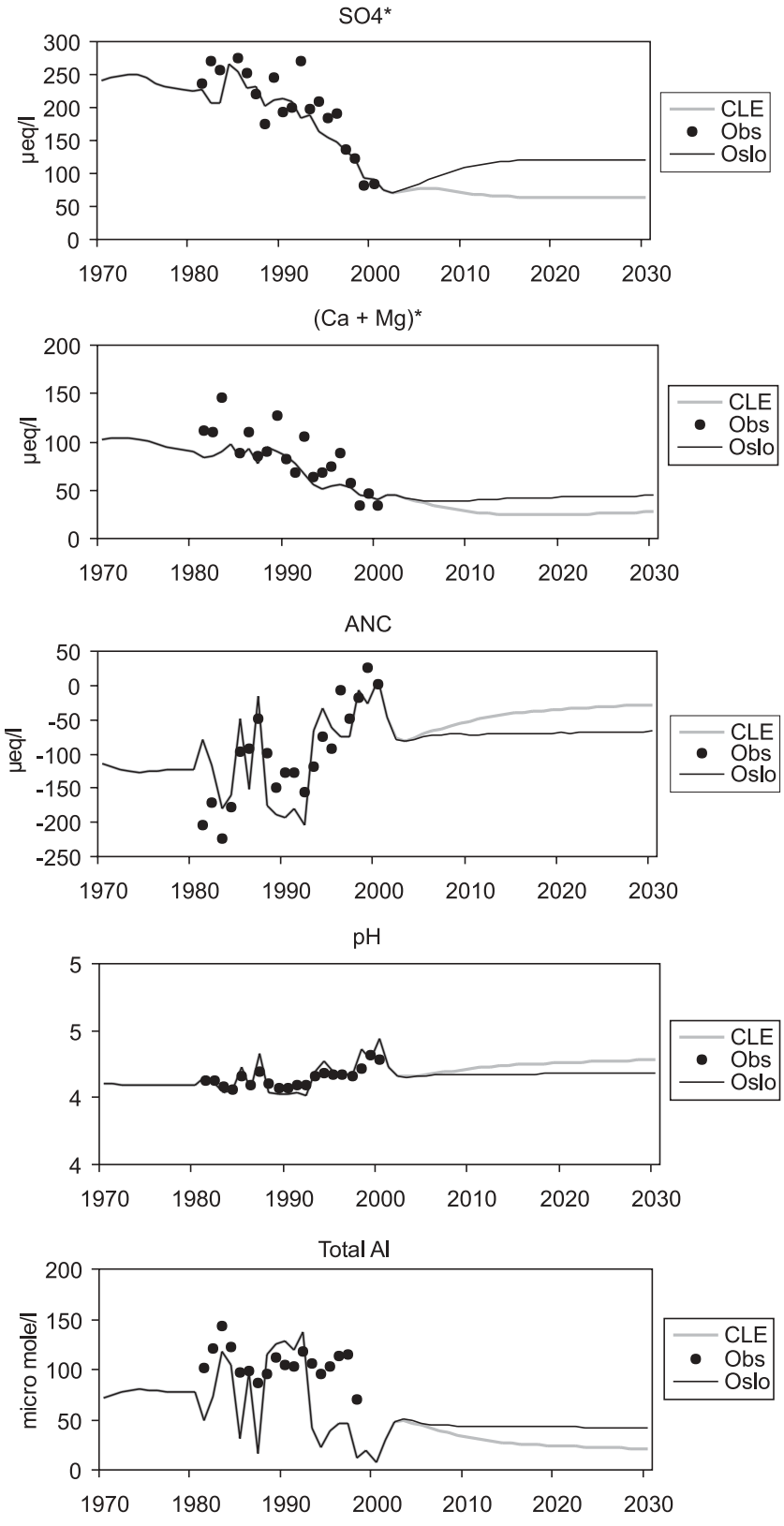

***Figure 7**. Simulated and observed surface water chemistry and predictions under the Current Legislation (CLE) and Oslo Protocol scenarios at Gårdsjön.*

4 Model Uncertainties

The MAGIC model has been rigorously tested here against long-term observations of water chemistry and found to closely match observed trends in most cases. This work needs to be advanced to consider the reasons for mismatches in observed and predicted trends (e.g. at Hietajärvi) and to explore key sensitivities in the model (e.g. S adsorption at Forellenbach) and its input data with a view to quantifying uncertainty in the prediction. Key uncertainties have been identified in relation to the current understanding of future N dynamics in terrestrial systems and changing sea-salt inputs as a result of the influence of global change.

Future nitrogen dynamics as confounding factor

As deposition of S is decreasing in Europe, the relative importance of N is increasing as the reduction of N-emissions is very small compared to reductions in S-emissions. If all deposited N leached to surface waters as NO_3, this would in many areas contribute as strongly to acidification as anthropogenic SO_4. However, most terrestrial systems are N-limited and consequently have a pronounced retention of inorganic N. When N-deposition exceeds uptake capacities, and/or root damage caused by acidification reduces N-uptake capacities, NO_3 concentrations in runoff water are expected to increase (Aber *et al*. 1989, Stoddard 1994).

The hypothesis which is taken into consideration for the Gothenburg protocol through application of the steady-state FAB model used for estimating critical loads of S and N, suggests that all N-deposition over a certain catchment-specific threshold value will leach out in runoff water at some stage in the future (Henriksen and Posch 2001). This leakage is the potential contribution of N to acidification. Today most catchments retain far more N than this hypothesis would suggest. In southern Norway for instance, the retention is typically between 5% and 30%, decreasing from the south-west to the north-east (Larssen *et al*. 2001). The extent of N retention in the future, and consequently the future influence of N on surface water acidification, therefore, represents a key uncertainty in future recovery from acidification.

The effect of this uncertainty can be captured in model applications by assuming 'best' and 'worst' cases of N behaviour in the future (Figure 8). At Birkenes, two N scenarios describe the best and worst cases under the Gothenburg Protocol emission reductions beyond 2010:

(i) a best case assuming N will be retained at the same relative proportion to the input as observed at present, i.e. constant proportional N retention, and;
(ii) a linear decrease in the net N retention to zero in 2090 (Figure 8).

The impact of this is linear increase in the NO_3 concentration and thus a decrease in ANC (Figure 8). The decrease is substantial; it may prevent further recovery and as a worst case cause re-acidification even after implementing the agreed emission reductions.

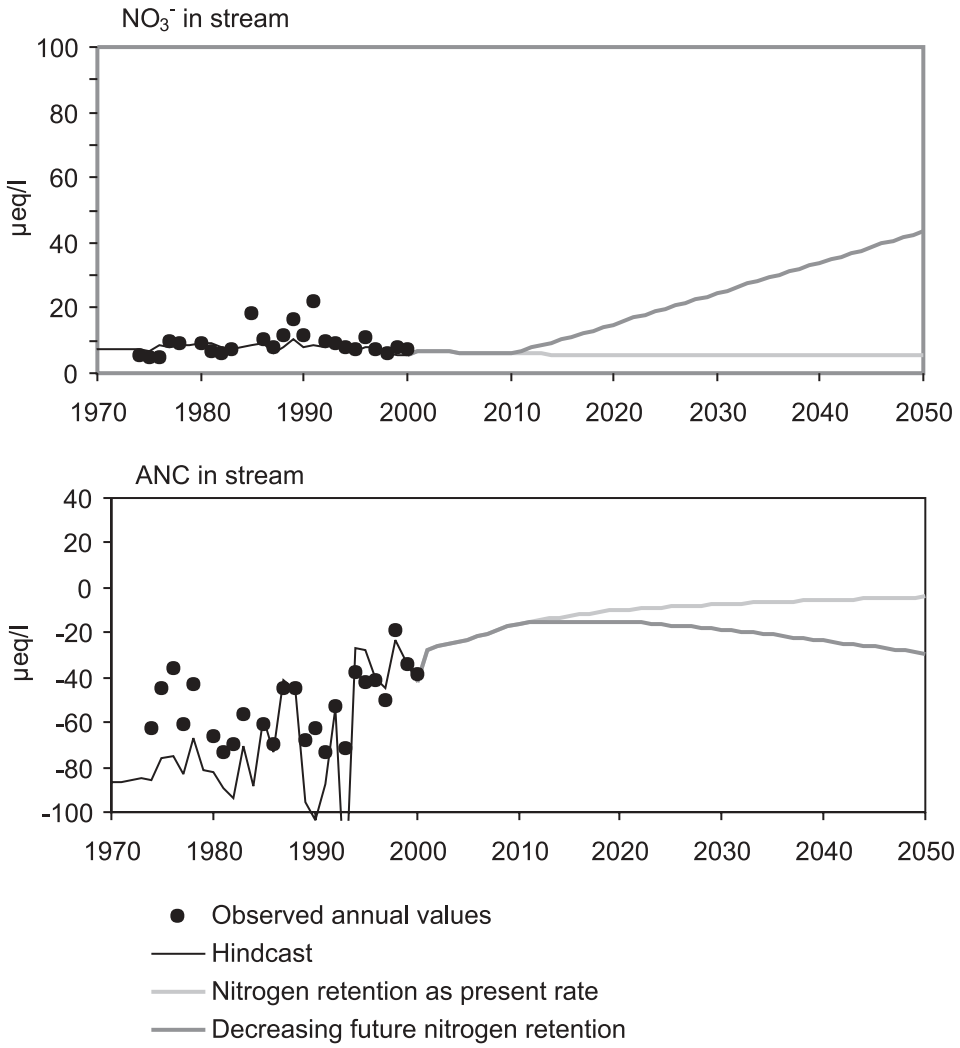

***Figure 8**. Illustration of the impact of future changes in the catchment nitrogen retention for surface water at Birkenes assuming nitrogen leakage increasing linearly from present level to full leakage between 2010 and 2090.*

Sea-salt episodes as confounding factor

Sea salt episodes are well known to have an impact on surface water chemistry (Hindar *et al*. 1994). The driving process is Na and Mg in sea salt enriched rainwater mobilising potentially toxic Al in the catchment. This mobilisation is most severe a few days or weeks after the sea salt event, but can also be seen in the annual average data. The possible impacts of sea salts in the future can be identified and characterised by using the deposition and runoff observations for the period 1974 to 2000 to assess sea salt impacts in the past and then to extrapolate this pattern into the future (Figure 9). Two particularly severe sea salt episodes were observed in 1991 and 1993 in southern Norway, and the peaks in the chemistry for these years can be seen repeated in the hindcast and forecasts (Figure 9).

Two forecast scenarios have been examined; both based on the CLE scenario deposition, but differing in the assumed forecast scenario for sea salts. In one scenario the observed variation was repeated into the future and in the other scenario observed sea salt deposition is increased by 50%. This scenario is an extreme simplification to illustrate the possible case of increased event frequency (implying increased total sea salt deposition).

For the standard scenario, the model run suggests that the dip in ANC observed with sea salt events will be smaller as the acidification pressure decreases (Figure 9). The model run also illustrates the large variation from year to year, related to the variation in sea salt inputs. For the scenario with increased sea salt deposition (illustrated with Cl^- in Figure 9) soil base saturation is predicted to increase faster than for the standard scenario. The ANC is lower in the beginning, but as the base saturation builds up faster, so the difference in ANC between the two scenarios decreases. Similar results are reported from other sites in Scandinavia (Beier *et al.* 2003).

Uncertainties in predictions

Two major confounding factors, future N dynamics and the impact of sea salt events, were discussed above. The future dynamics of these two are important sources of uncertainty in the model predictions. There are also, however, uncertainties related to the model input and calibration data. The extensive data available from the ICP catchments are of great value in exploring the predictive power of dynamic models and to evaluate the uncertainties in predictions.

Data from Birkenes have been used in order to explore how uncertainties in predictions can be quantified (Larssen *et al*. 2002). Some of the results are included here in order to illustrate that uncertainties can be quantified and to show how they compare in size with the confounding factors discussed above. A large number of model calibrations were conducted in a Monte-Carlo framework to give several thousand different sets of model inputs. The model outputs were refined by stepwise addition of information from the time series of observations available (Figure 10). The results presented here represent the refined outputs to the entire time series available. The outputs can be seen as a probability distribution of model predictions. The details on methodology, parameter selection and results are given in Larssen *et al.* (2002).

The inclusion of the year to year variation for sea salts and runoff rate result in a variation in the modelled SO_4 concentration which is much larger than the uncertainty band from the uncertainty study (Figure 10). This is because a smooth long-term average is assumed when setting the uncertainty for SO_4 deposition in the inputs. The modelled Ca concentration, when including the sea salts, is within the uncertainty band for most years, except the most extreme sea salt years. The situation is similar for the modelled ANC: the variation caused by the sea salt inclusion is moderate compared to the uncertainty band and only falls below the minimum line in the extreme sea salt years.

The uncertainty in the forecast related to future retention of N, according to current knowledge, falls within the uncertainty caused by the other factors. The predicted ANC for 2050 for the changed N scenario is about the same as the predicted minimum value from the uncertainty study.

This comparison of the magnitude of the uncertainty related to the inputs in general, the N dynamics and the sea salt deposition dynamics show they are predicted to be of similar magnitude (Figure 10).

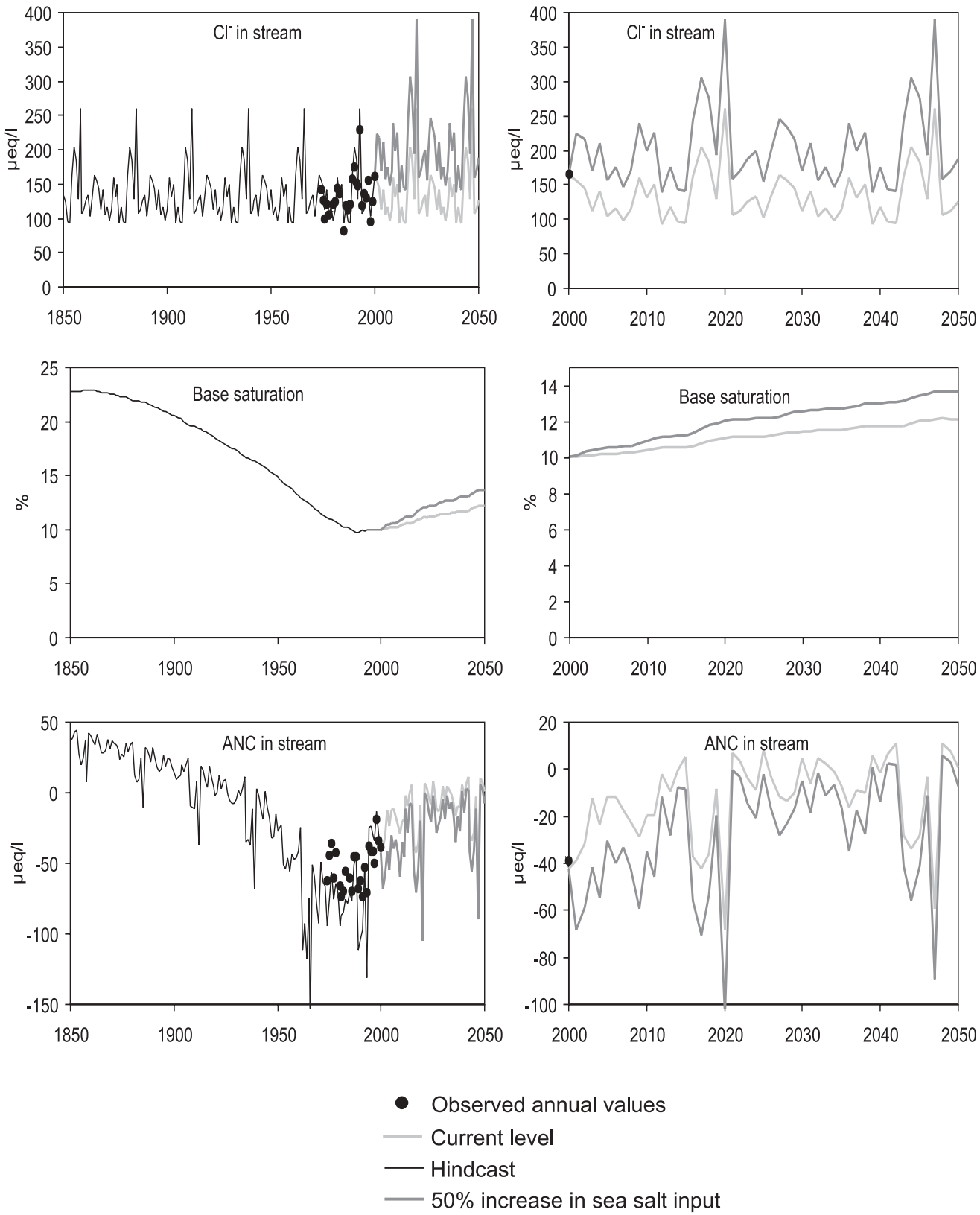

***Figure 9**. Illustration of the impact of sea salt variation included in the model run. The natural variation in sea salt deposition observed for the period 1974-2000 is repeated through the entire time series of deposition and annual runoff amount used as model inputs. Two different scenarios are run; one repeating the observed sea salt pattern in the future, another with 50% increased sea salt deposition. The panels to the left show the entire time period 1850 to 2050, while the panels to the right show the time segment from 2000 to 2050.*

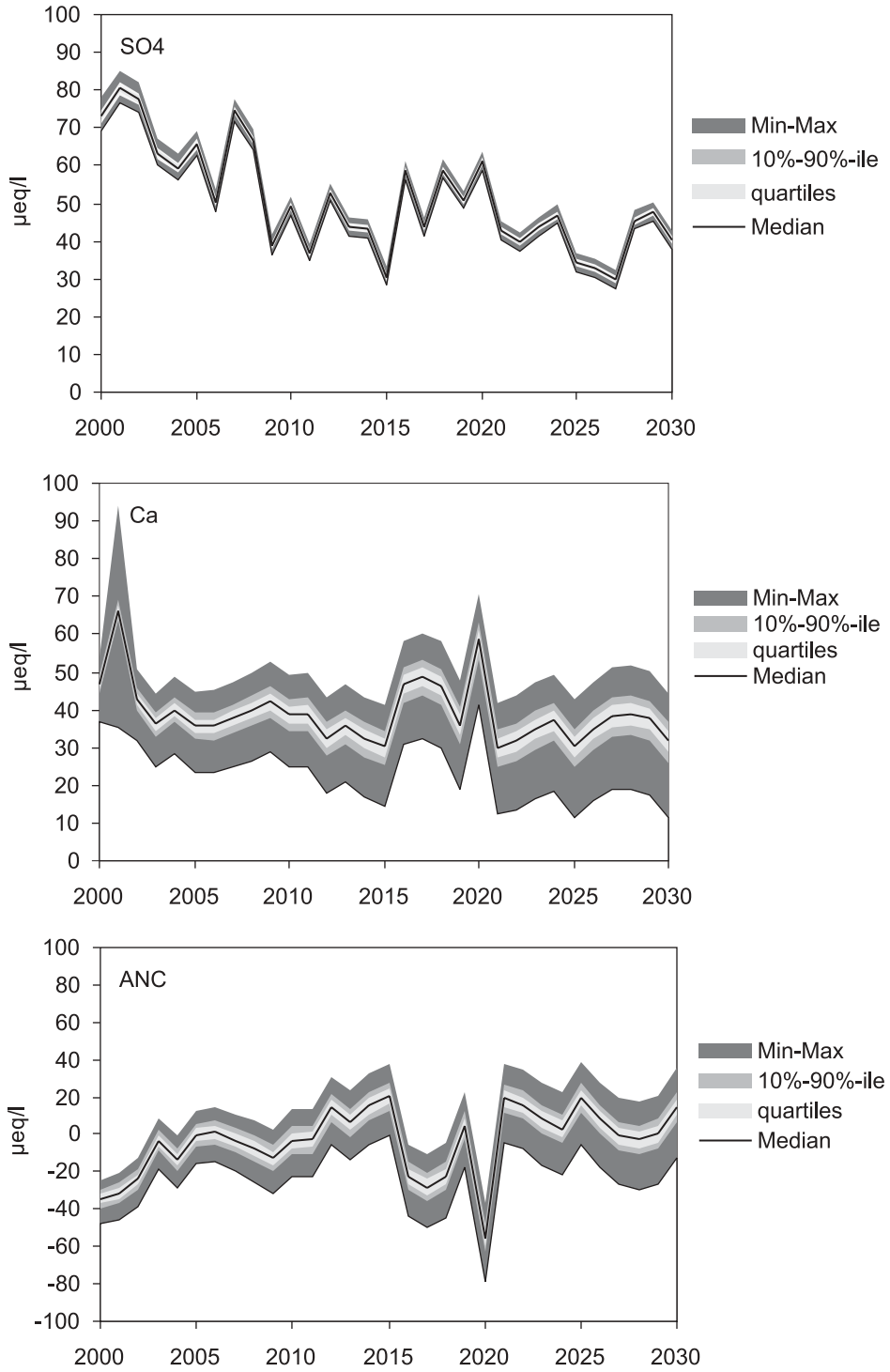

***Figure 10**. Illustration of uncertainties in model predictions (Larssen* et al. *2002), where uncertainties in inputs and parameter estimates are combined with the modelled variation due to sea salt events (Figure 9) and the uncertainty related to the fate of nitrogen in the future (Figure 8).*

5 Future Requirements

There exist significant areas of research to elucidate our current understanding in relation to S and N dynamics. In terms of S dynamics, some sites (Hietajärvi and Forellenbach) indicated a mismatch in observed input and output fluxes during the period of S deposition decline which can only be reproduced by invoking S adsorption on catchment soils in the model. The magnitude of this pool and its nature remain largely unknown. For example, does the adsorption in MAGIC represent enough chemical retention of SO_4, a reduction of SO_4 in wetlands or incorporation of S into an organic S pool (Alewell *et al.* 2001)? All of these S retention mechanisms are different chemical processes and indeed all three may operate in a catchment. The degree to which the 'Langmuir isotherm' used in MAGIC can model the adsorption and release of S remains a key question. Further experimental studies and long-term monitoring are required to solve this problem (Alewell *et al.* 2001, Prechtel *et al.* 2001).

With regard to the current understanding of long-term N retention and leakage, the response of soils is now well known and documented (e.g. Gundersen 1998) from experimental studies but there exists no convincing trends to increased N leaching in long-term surface water chemistry data (Wright *et al.* 2001). At catchment scale, it is likely that different soils will behave differently with respect to N retention/release which may tend to mask any long-term changes. In addition, there are key uncertainties in determining the C and N pools at catchment scale to parameterise the model. Further monitoring of soils and surface waters both spatially and through time will provide important new information against which to test our current understanding and the process representation included in the MAGIC model (e.g. Jenkins *et al.* 2001).

The ICP IM database provides considerable possibility for furthering the dynamic modelling effort in support of the Convention. So far, no attempt has been made to link chemical model outputs with biological observations at the sites. In addition, there exist many sites where data suitable for dynamic model application exist. These would potentially provide an extensive range of biogeochemical conditions against which to test model performance, sensitivity/uncertainty and response to agreed emission reductions.

6 Conclusions

Long-term observations of input and output chemistry at intensively monitored catchments provides an important test of the performance of dynamic models. Furthermore, the detailed soil physical and chemical data available for these sites provide for a 'best' assessment of model parameters (for example compared to survey data). This makes these model applications as representative as can be expected. In all cases detailed here, the MAGIC model was more or less capable of matching the observations of stream chemistry over a ten (or more) year time period. The ability of the model to capture observed long-term responses provides confidence in model predictions under emission scenarios into the future.

In addition, European scale dynamic modelling assessment is likely to focus on chemistry data from wide regional surveys of surface waters (Jenkins *et al.* 2002). These surveys often comprise of single water samples from many sites collected many years apart. Also, detailed soil information is rarely available at this scale and so soil characteristics are derived from mapping using extrapolation techniques (Helliwell *et al.* 1998). Clearly, detailed model applications to any one site in these regions provides a 'reference' for the regional modelling. This defines the role of the ICP IM with respect to dynamic modelling assessment and establishes the need for strong links to ICP Waters and other national/regional modelling efforts.

Sensitivity analysis is urgently required with respect to the model predictions and the value of the detailed, site specific, model applications is clear in this respect. The need for continued long-term monitoring at the ICP IM catchments is clear and the current effort must be maintained.

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